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1/22/07
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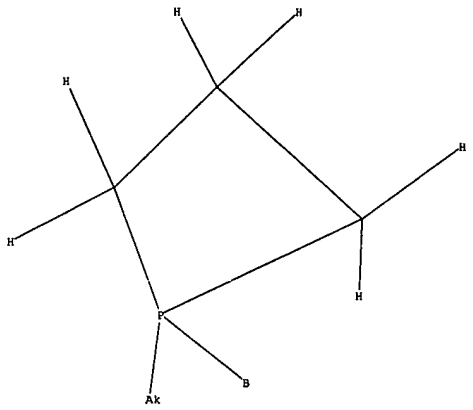

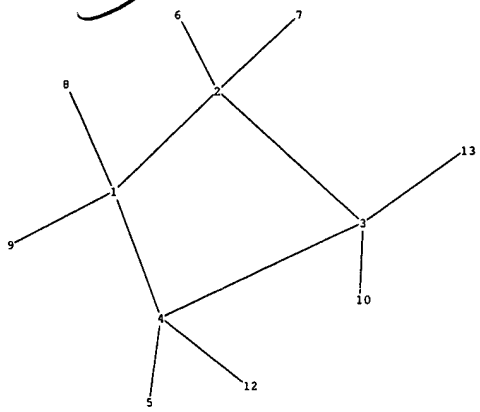

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5 6 7 8 9 10 12 13
ring nodes :
1 2 3 4
chain bonds :
1-8 1-9 2-6 2-7 3-10 3-13 4-5 4-12
ring bonds :
1-2 1-4 2-3 3-4
exact/norm bonds :
1-2 1-4 2-3 3-4 4-5
exact bonds :
1-8 1-9 2-6 2-7 3-10 3-13 4-12

G1:O,S

Match level :
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10:CLASS 12:CLASS 13:CLASS

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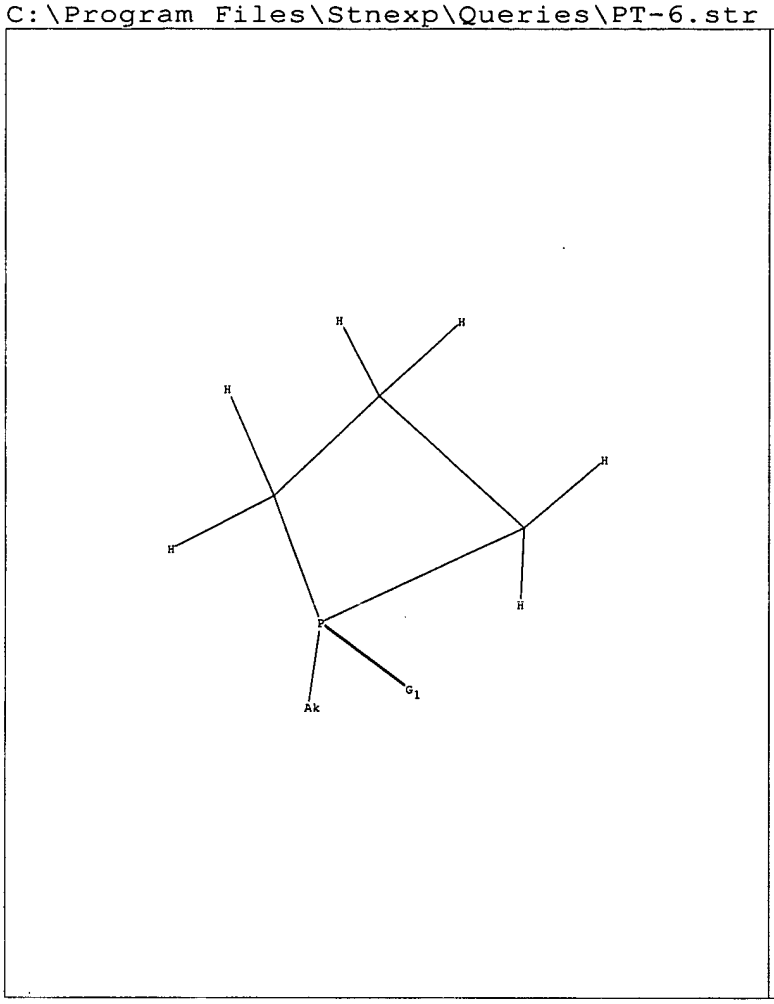

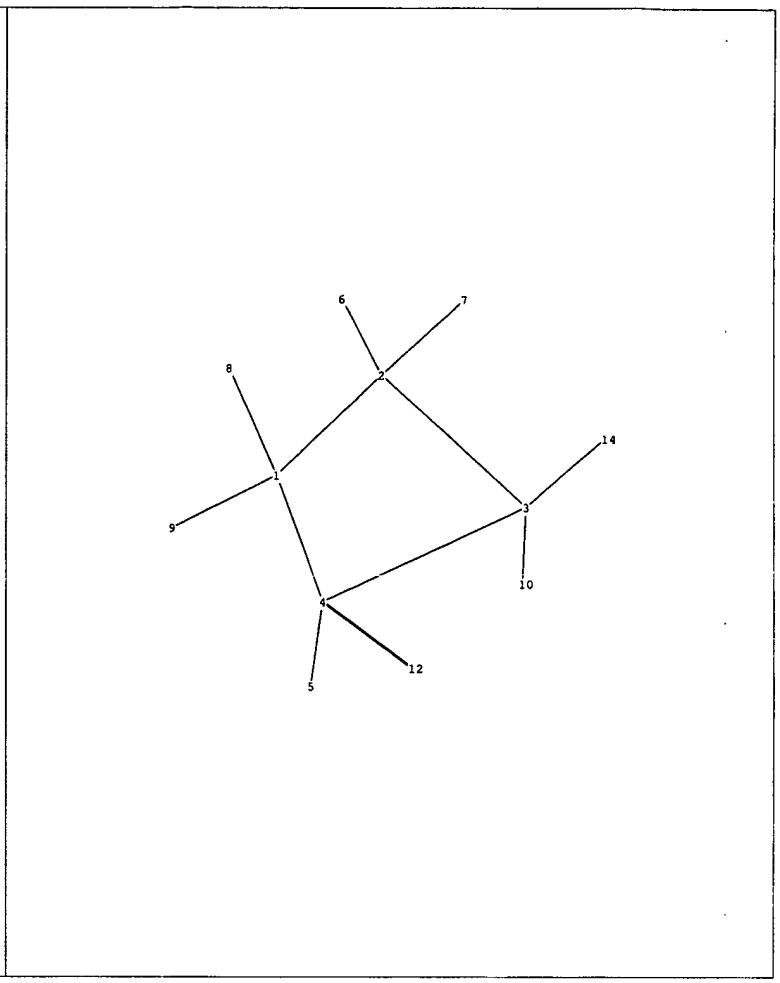

chain nodes :
5 6 7 8 9 10 12 14
ring nodes :
1 2 3 4
chain bonds :
1-8 1-9 2-6 2-7 3-10 3-14 4-5 4-12
ring bonds :
1-2 1-4 2-3 3-4
exact/norm bonds :
1-2 1-4 2-3 3-4 4-5 4-12
exact bonds :
1-8 1-9 2-6 2-7 3-10 3-14

G1:O,S

Match level :
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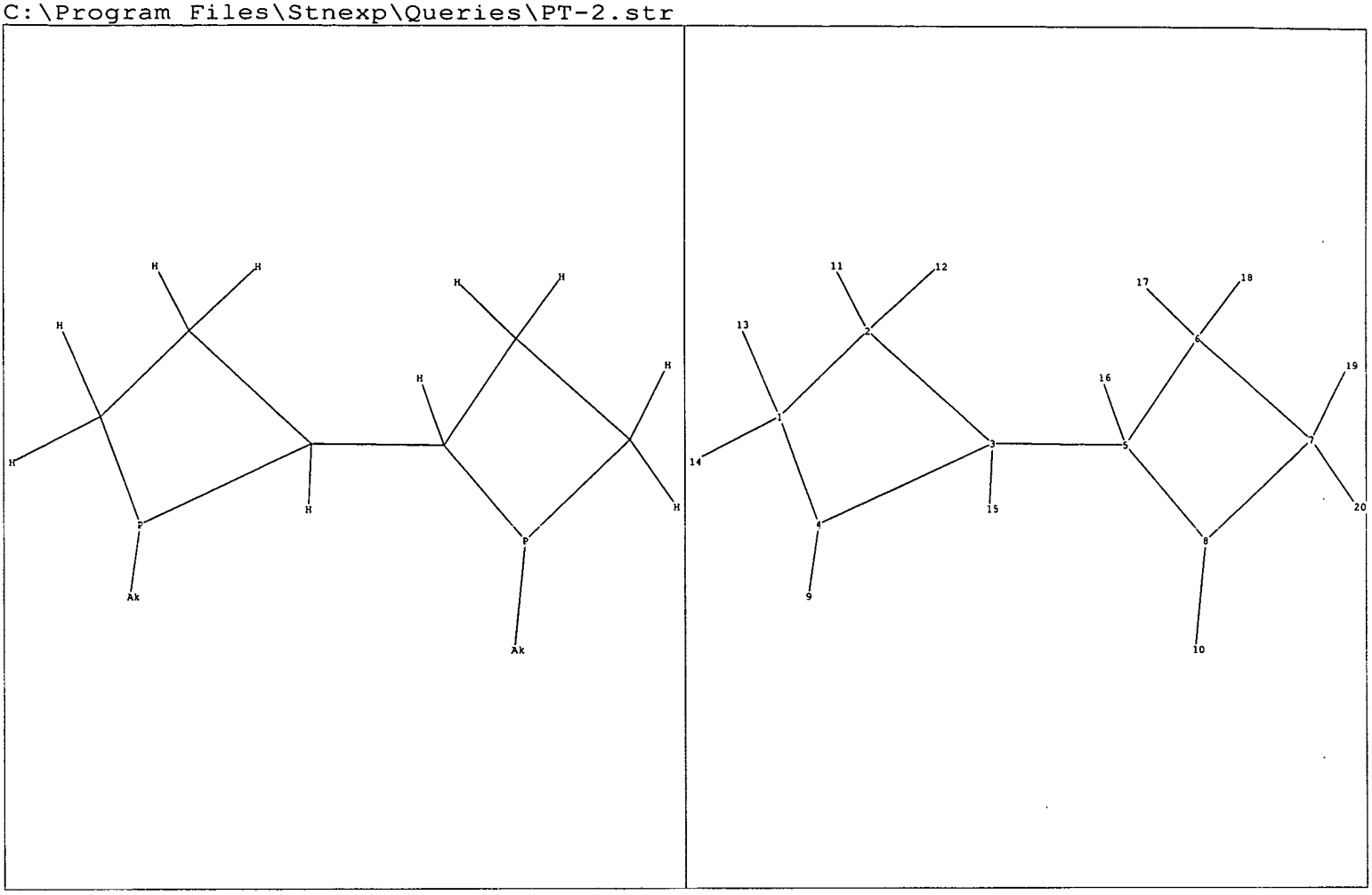
10:CLASS 12:CLASS 14:CLASS

C:\Program Files\Stnexp\Queries\PT-2.str



chain nodes :
9 10 11 12 13 14 15 16 17 18 19 20
ring nodes :
1 2 3 4 5 6 7 8
chain bonds :
1-13 1-14 2-11 2-12 3-5 3-15 4-9 5-16 6-17 6-18 7-19 7-20 8-10
ring bonds :
1-2 1-4 2-3 3-4 5-6 5-8 6-7 7-8
exact/norm bonds :
1-2 1-4 2-3 3-4 4-9 5-6 5-8 6-7 7-8 8-10
exact bonds :
1-13 1-14 2-11 2-12 3-5 3-15 5-16 6-17 6-18 7-19 7-20

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:CLASS
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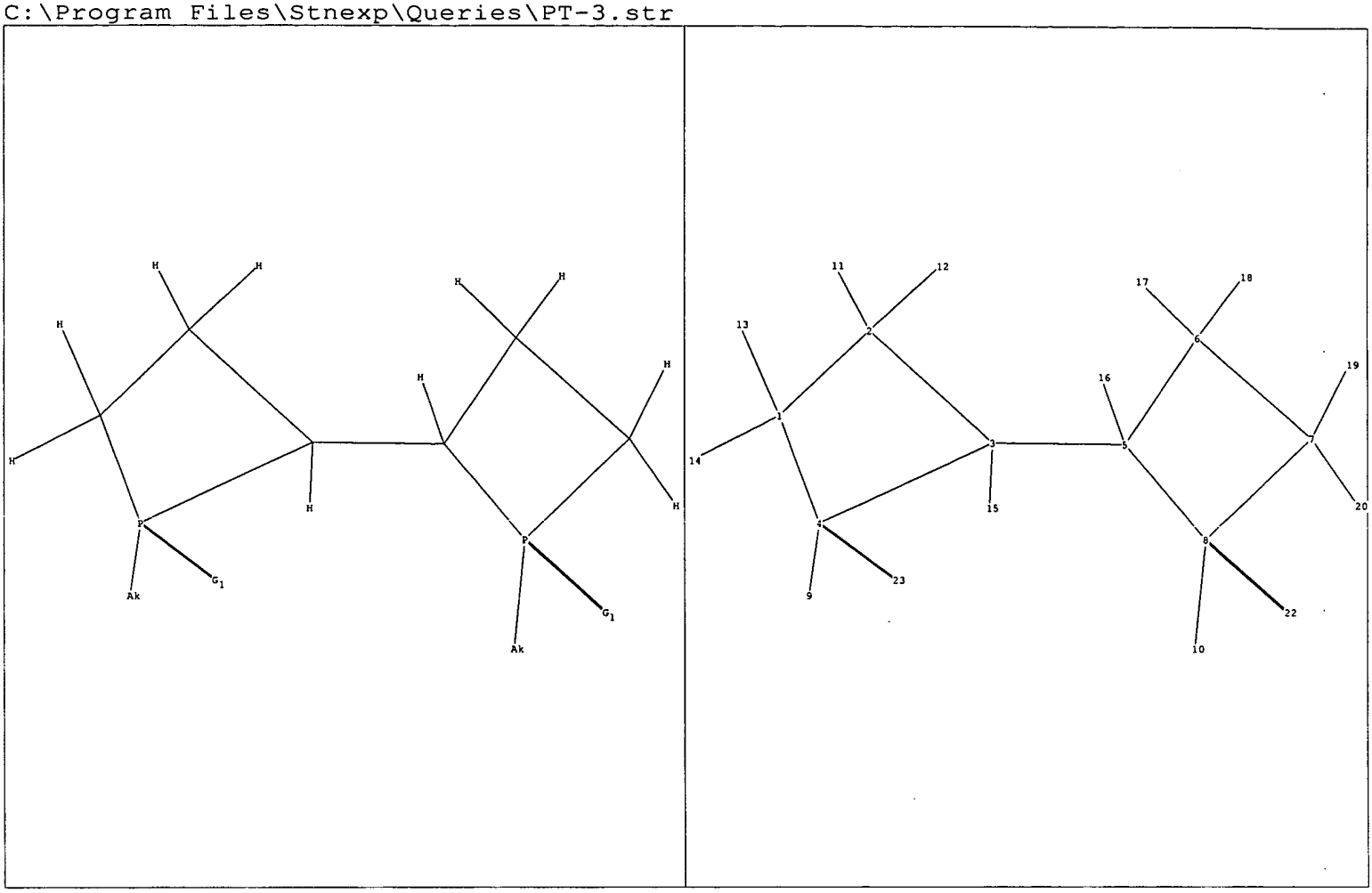
17:CLASS 18:CLASS 19:CLASS 20:CLASS

C:\Program Files\Stnexp\Queries\PT-3.str



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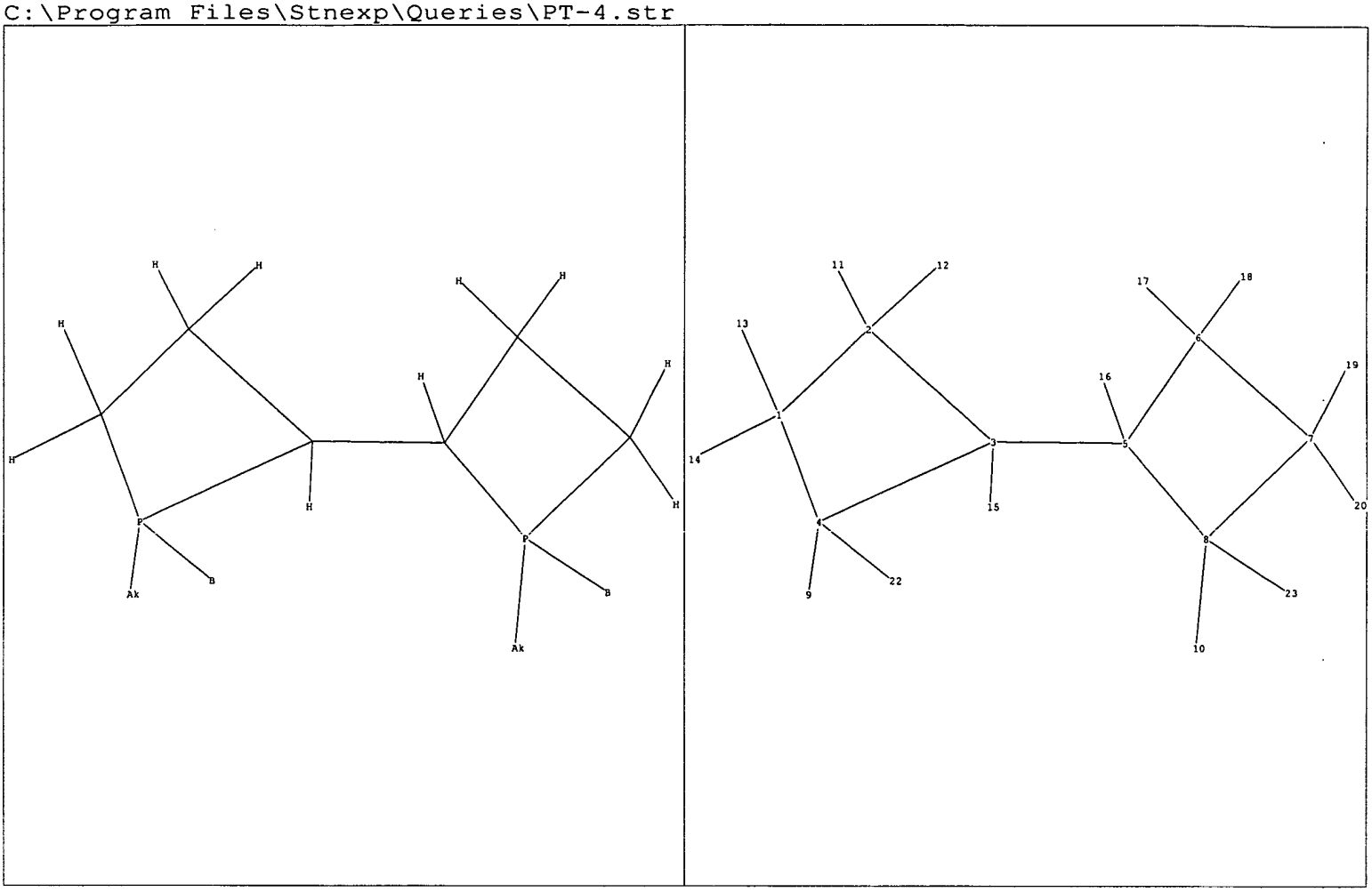
ring nodes :
1 2 3 4 5 6 7 8
chain bonds :
1-13 1-14 2-11 2-12 3-5 3-15 4-9 4-23 5-16 6-17 6-18 7-19 7-20
8-10 8-22
ring bonds :
1-2 1-4 2-3 3-4 5-6 5-8 6-7 7-8
exact/norm bonds :
1-2 1-4 2-3 3-4 4-9 4-23 5-6 5-8 6-7 7-8 8-10 8-22
exact bonds :
1-13 1-14 2-11 2-12 3-5 3-15 5-16 6-17 6-18 7-19 7-20

G1:O,S

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:CLASS
10:CLASS 11:CLASS 12:CLASS 13:CLASS 14:CLASS 15:CLASS 16:CLASS
17:CLASS 18:CLASS 19:CLASS 20:CLASS 22:CLASS 23:CLASS

C:\Program Files\Stnexp\Queries\PT-4.str



chain nodes :
9 10 11 12 13 14 15 16 17 18 19 20 22 23
ring nodes :
1 2 3 4 5 6 7 8
chain bonds :
1-13 1-14 2-11 2-12 3-5 3-15 4-9 4-22 5-16 6-17 6-18 7-19 7-20
8-10 8-23
ring bonds :
1-2 1-4 2-3 3-4 5-6 5-8 6-7 7-8
exact/norm bonds :
1-2 1-4 2-3 3-4 4-9 5-6 5-8 6-7 7-8 8-10
exact bonds :
1-13 1-14 2-11 2-12 3-5 3-15 4-22 5-16 6-17 6-18 7-19 7-20 8-23

G1:O,S

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:CLASS
10:CLASS 11:CLASS 12:CLASS 13:CLASS 14:CLASS 15:CLASS 16:CLASS
17:CLASS 18:CLASS 19:CLASS 20:CLASS 22:CLASS 23:CLASS

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

FILE COVERS 1907 - 22 Jan 2007 VOL 146 ISS 5
FILE LAST UPDATED: 21 Jan 2007 (20070121/ED)

Effective October 17, 2005, revised CAS Information Use Policies apply. They are available for your review at:

http://www.cas.org/infopolicy.html

=> D L1
L1 HAS NO ANSWERS
L1 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.

=> S L1 FULL
REG1stRY INITIATED
Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

FULL SEARCH INITIATED 10:14:59 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 283 TO ITERATE

100.0% PROCESSED 283 ITERATIONS 2 ANSWERS
SEARCH TIME: 00.00.01

L3 2 SEA SSS FUL L1

L4 3 L3

=> D L4 IBIB ABS HITSTR 1-3

L4 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2005:99512 CAPLUS
DOCUMENT NUMBER: 142:198205
TITLE: Process for producing optically active dimer of phosphorus heterocycle
INVENTOR(S): Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S): Nippon Chemical Industrial Co., Ltd., Japan
SOURCE: PCT Int. Appl., 42 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent

LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005010014	A1	20050203	WO 2004-JP10671	20040727
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1650216	A1	20060426	EP 2004-747983	20040727
R: CH, DE, GB, LI				
US 2006211888	A1	20060921	US 2006-564985	20060118
PRIORITY APPLN. INFO.:			JP 2003-280584 A	20030728
			WO 2004-JP10671 W	20040727

OTHER SOURCE(S): MARPAT 142:198205
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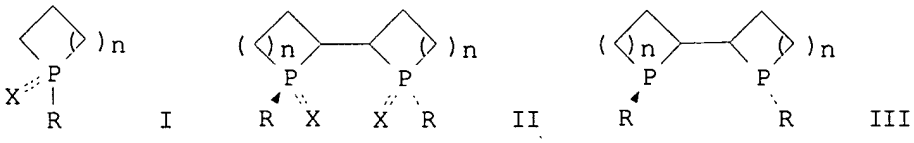
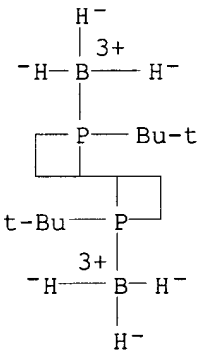


AB A compound represented by the following general formula Y-CnH2n-Y (wherein Y = halogeno or a leaving group selected among -OTs, -OTf, and -OMs; n = a number of 3 to 6) is caused to act on a primary phosphine represented by the following general formula R-PH2 (wherein R = linear, branched, or cyclic C2-20 alkyl) in the presence of a base. Subsequently, boron trihydride, oxygen, or sulfur is caused to act thereon to obtain a heterocyclic phosphorus compound represented by the following general formula (I) (wherein R = the same as defined above; n = a number of 1 to 4; X = a boron trihydride group, oxygen, or sulfur; and = = = indicates a single bond when X is a boron trihydride group, and indicates a double bond when X is oxygen or sulfur). The compound I is dimerized to obtain a dimer of the heterocyclic phosphorus compound, the dimer being a diphosphetane represented by the following general formula (II) (wherein R, n, and X are the same as defined above). Subsequently, the phosphorus heterocycle dimer II is subjected to deoxidn., desulfurization, or borane elimination to obtain an optically active phosphorus heterocycle dimer represented by the following general formula (III) (wherein R and n are the same as defined above). These diphosphetanes III build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a

solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over 2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% III (R = tert-butyl). III (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol [rhodium(I)bis (norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice, 20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

IT 735288-29-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)

RN 735288-29-6 CAPLUS
CN Boron, [μ-[(1S,1'S,2R,2'R)-1,1'-bis(1,1-dimethylethyl)-2,2'-biphosphetane-κP1:κP1']]hexahydrodi- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2005:99511 CAPLUS
DOCUMENT NUMBER: 142:198204
TITLE: Preparation of novel optically active phosphorus-chiral diphosphetanes, intermediates of the same, and transition metal complexes containing the diphosphetanes as the ligand
INVENTOR(S): Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S): Nippon Chemical Industrial Co., Ltd., Japan
SOURCE: PCT Int. Appl., 31 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.		DATE
WO 2005010013	A1	20050203	WO 2004-JP10670		20040727
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW					
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG					
EP 1650217	A1	20060426	EP 2004-770961		20040727
R: CH, DE, GB, LI					
US 2006189818	A1	20060824	US 2006-564984		20060118
PRIORITY APPLN. INFO.:			JP 2003-280584	A	20030728
			WO 2004-JP10670	W	20040727

OTHER SOURCE(S): MARPAT 142:198204
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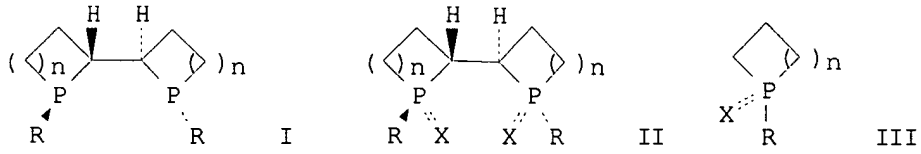
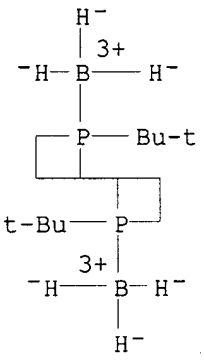


AB Novel optically active phosphorus-chiral diphosphetanes (I) (R = C2-20 straight-chain, branched, or cyclic alkyl) and intermediates of the same (II) and (III) (R = same as above; X = BH3, O, S; the double dotted line = a single bond when X = BH3 or a double bond when X = O or S), and transition metal complex catalysts containing the diphosphetanes as the ligand I are prepared These diphosphetanes build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over 2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% I (R = tert-butyl). I (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol

[rhodium(I)bis(norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice, 20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

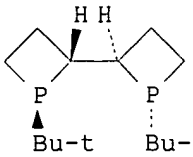
IT 735288-29-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of novel optically active phosphorus-chiral diphosphetanes and transition metal complexes thereof for catalytic asym. syntheses such as asym. hydrogenation)

RN 735288-29-6 CAPLUS
CN Boron, [μ-[(1S,1'S,2R,2'R)-1,1'-bis(1,1-dimethylethyl)-2,2'-biphosphetane-κP1:κP1']]hexahydrodi- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2004:536413 CAPLUS
DOCUMENT NUMBER: 141:174232
TITLE: Optically active 1,1'-di-tert-butyl-2,2'-diphosphetanyl and its application in rhodium-catalyzed asymmetric hydrogenations
AUTHOR(S): Imamoto, Tsuneo; Oohara, Nobuhiko; Takahashi, Hidetoshi
CORPORATE SOURCE: Department of Chemistry, Faculty of Science, Chiba University, Chiba, 263-8522, Japan
SOURCE: Synthesis (2004), (9), 1353-1358
CODEN: SYNTBF; ISSN: 0039-7881
PUBLISHER: Georg Thieme Verlag
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 141:174232
GI



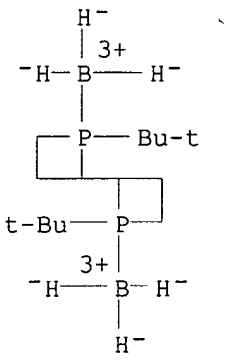
I

AB (1S,1'S,2R,2'R)-1,1'-Di-tert-butyl-2,2'-diphosphetanyl (I) was prepared from tert-butylphosphine via phosphine-boranes as intermediates. The rhodium complex of the ligand was used as a highly efficient catalyst in asym. hydrogenations of α-acetyl-aminoacrylates and α-substituted enamides.

IT 735288-29-6P
RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(stereoselective preparation and crystal structure of bis(phosphetane-borane) via heterocyclization of t-butylphosphine with dichloropropane followed by boronation and sparteine-catalyzed stereoselective dimerization in the preparation of DiSquareP*)

RN 735288-29-6 CAPLUS

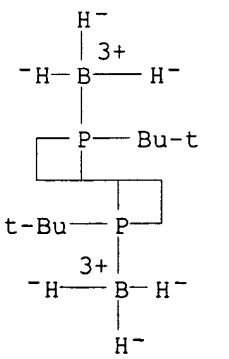
CN Boron, [μ-[(1S,1'S,2R,2'R)-1,1'-bis(1,1-dimethylethyl)-2,2'-biphosphetane-κP1:κP1']]hexahydrodi- (9CI) (CA INDEX NAME)



IT 736140-19-5P
RL: SPN (Synthetic preparation); PREP (Preparation)
(stereoselective preparation of di(t-butyl)diphosphetanyl diborane via heterocyclization of t-butylphosphine with dichloropropane followed by addition of borane and sparteine-catalyzed stereoselective dimerization)

RN 736140-19-5 CAPLUS

CN Boron, [μ-[rel-(1R,1'S,2S,2'R)-1,1'-bis(1,1-dimethylethyl)-2,2'-biphosphetane-κP1:κP1']]hexahydrodi- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

FILE COVERS 1907 - 22 Jan 2007 VOL 146 ISS 5
FILE LAST UPDATED: 21 Jan 2007 (20070121/ED)

Effective October 17, 2005, revised CAS Information Use Policies apply. They are available for your review at:

http://www.cas.org/infopolicy.html

=> D L1
L1 HAS NO ANSWERS
L1 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.

=> S L1 FULL
REG1stRY INITIATED
Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

FULL SEARCH INITIATED 10:03:52 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 63 TO ITERATE

100.0% PROCESSED 63 ITERATIONS 2 ANSWERS
SEARCH TIME: 00.00.01

L3 2 SEA SSS FUL L1

L4 3 L3

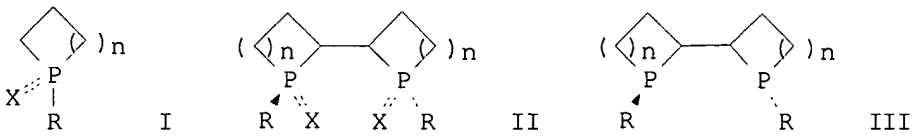
=> D L4 IBIB ABS HITSTR

L4 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2005:99512 CAPLUS
DOCUMENT NUMBER: 142:198205
TITLE: Process for producing optically active dimer of phosphorus heterocycle
INVENTOR(S): Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S): Nippon Chemical Industrial Co., Ltd., Japan
SOURCE: PCT Int. Appl., 42 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent

LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005010014	A1	20050203	WO 2004-JP10671	20040727
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1650216	A1	20060426	EP 2004-747983	20040727
R: CH, DE, GB, LI				
US 2006211888	A1	20060921	US 2006-564985	20060118
PRIORITY APPLN. INFO.:			JP 2003-280584 A	20030728
			WO 2004-JP10671 W	20040727

OTHER SOURCE(S): MARPAT 142:198205
GI



AB A compound represented by the following general formula Y-CnH2n-Y (wherein Y = halogeno or a leaving group selected among -OTs, -OTf, and -OMs; n = a number of 3 to 6) is caused to act on a primary phosphine represented by the following general formula R-PH2 (wherein R = linear, branched, or cyclic C2-20 alkyl) in the presence of a base. Subsequently, boron trihydride, oxygen, or sulfur is caused to act thereon to obtain a heterocyclic phosphorus compound represented by the following general formula (I) (wherein R = the same as defined above; n = a number of 1 to 4; X = a boron trihydride group, oxygen, or sulfur; and = = = indicates a single bond when X is a boron trihydride group, and indicates a double bond when X is oxygen or sulfur). The compound I is dimerized to obtain a dimer of the heterocyclic phosphorus compound, the dimer being a diphosphetane represented by the following general formula (II) (wherein R, n, and X are the same as defined above). Subsequently, the phosphorus heterocycle dimer II is subjected to deoxidn., desulfurization, or borane elimination to obtain an optically active phosphorus heterocycle dimer represented by the following general formula (III) (wherein R and n are the same as defined above). These diphosphetanes III build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and

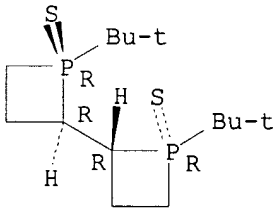
purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a

solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over 2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% III (R = tert-butyl). III (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol [rhodium(I)bis (norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice, 20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

IT 735288-40-1P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)

RN 735288-40-1 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'R,2R,2'R)- (9CI) (CA INDEX NAME)

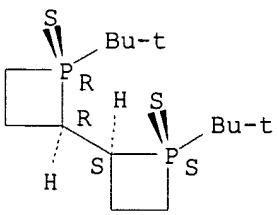
Absolute stereochemistry. Rotation (-).



IT 735288-42-3P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)

RN 735288-42-3 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'S,2S,2'R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

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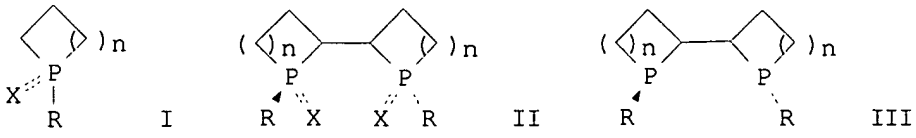
1-3 IS NOT A RECOGNIZED COMMAND
The previous command name entered was not recognized by the system.
For a list of commands available to you in the current file, enter
"HELP COMMANDS" at an arrow prompt (=>).

=> D L4 IBIB ABS HITSTR 1-3

L4 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2005:99512 CAPLUS
DOCUMENT NUMBER: 142:198205
TITLE: Process for producing optically active dimer of phosphorus heterocycle
INVENTOR(S): Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S): Nippon Chemical Industrial Co., Ltd., Japan
SOURCE: PCT Int. Appl., 42 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005010014	A1	20050203	WO 2004-JP10671	20040727
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1650216	A1	20060426	EP 2004-747983	20040727
R: CH, DE, GB, LI				
US 2006211888	A1	20060921	US 2006-564985	20060118
PRIORITY APPLN. INFO.:			JP 2003-280584 A	20030728
			WO 2004-JP10671 W	20040727

OTHER SOURCE(S): MARPAT 142:198205
GI



AB A compound represented by the following general formula Y-CnH2n-Y (wherein Y = halogeno or a leaving group selected among -OTs, -OTf, and -OMs; n = a number of 3 to 6) is caused to act on a primary phosphine represented by the following general formula R-PH2 (wherein R = linear, branched, or cyclic C2-20 alkyl) in the presence of a base. Subsequently, boron trihydride, oxygen, or sulfur is caused to act thereon to obtain a heterocyclic phosphorus compound represented by the following general formula (I)

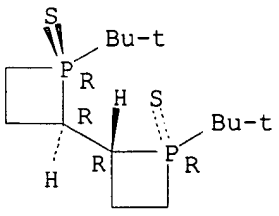
(wherein R = the same as defined above; n = a number of 1 to 4; X = a boron trihydride group, oxygen, or sulfur; and = = = indicates a single bond when X is a boron trihydride group, and indicates a double bond when X is oxygen or sulfur). The compound I is dimerized to obtain a dimer of the heterocyclic phosphorus compound, the dimer being a diphosphetane represented by the following general formula (II) (wherein R, n, and X are the same as defined above). Subsequently, the phosphorus heterocycle dimer II is subjected to deoxidn., desulfurization, or borane elimination to obtain an optically active phosphorus heterocycle dimer represented by the following general formula (III) (wherein R and n are the same as defined above). These diphosphetanes III build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over 2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% III (R = tert-butyl). III (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol [rhodium(I)bis (norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice, 20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

IT 735288-40-1P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)

RN 735288-40-1 CAPLUS

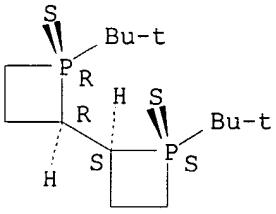
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'R,2R,2'R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



IT 735288-42-3P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)
RN 735288-42-3 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'S,2S,2'R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2005:99511 CAPLUS
DOCUMENT NUMBER: 142:198204
TITLE: Preparation of novel optically active phosphorus-chiral diphosphetanes, intermediates of the same, and transition metal complexes containing the diphosphetanes as the ligand
INVENTOR(S): Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S): Nippon Chemical Industrial Co., Ltd., Japan
SOURCE: PCT Int. Appl., 31 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.		DATE
WO 2005010013	A1	20050203	WO 2004-JP10670		20040727
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW					
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG					
EP 1650217	A1	20060426	EP 2004-770961		20040727
R: CH, DE, GB, LI					
US 2006189818	A1	20060824	US 2006-564984		20060118
PRIORITY APPLN. INFO.:			JP 2003-280584	A	20030728
			WO 2004-JP10670	W	20040727

OTHER SOURCE(S): MARPAT 142:198204
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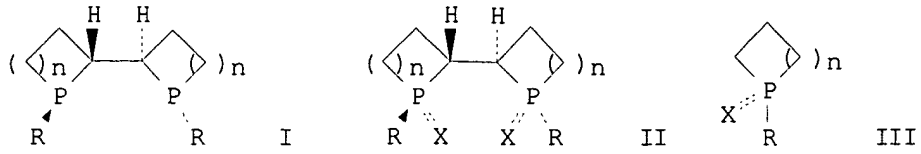


I II III

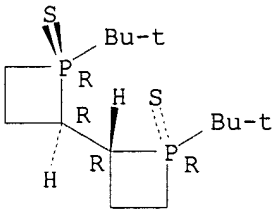
AB Novel optically active phosphorus-chiral diphosphetanes (I) (R = C2-20 straight-chain, branched, or cyclic alkyl) and intermediates of the same (II) and (III) (R = same as above; X = BH3, O, S; the double dotted line = a single bond when X = BH3 or a double bond when X = O or S), and transition metal complex catalysts containing the diphosphetanes as the ligand I are prepared These diphosphetanes build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over 2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% I (R = tert-butyl). I (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol [rhodium(I)bis(norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice, 20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

IT 735288-40-1P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of novel optically active phosphorus-chiral diphosphetanes and transition metal complexes thereof for catalytic asym. syntheses such as asym. hydrogenation)

RN 735288-40-1 CAPLUS

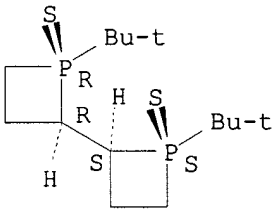
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'R,2R,2'R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



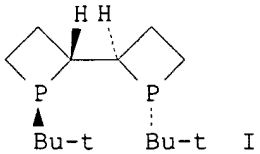
IT 735288-42-3P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of novel optically active phosphorus-chiral diphosphetanes and transition metal complexes thereof for catalytic asym. syntheses such as asym. hydrogenation)
RN 735288-42-3 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'S,2S,2'R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2004:536413 CAPLUS
DOCUMENT NUMBER: 141:174232
TITLE: Optically active 1,1'-di-tert-butyl-2,2'-diphosphetanyl and its application in rhodium-catalyzed asymmetric hydrogenations
AUTHOR(S): Imamoto, Tsuneo; Oohara, Nobuhiko; Takahashi, Hidetoshi
CORPORATE SOURCE: Department of Chemistry, Faculty of Science, Chiba University, Chiba, 263-8522, Japan
SOURCE: Synthesis (2004), (9), 1353-1358
CODEN: SYNTBF; ISSN: 0039-7881
PUBLISHER: Georg Thieme Verlag
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 141:174232
GI



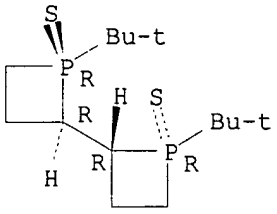
AB (1S,1'S,2R,2'R)-1,1'-Di-tert-butyl-2,2'-diphosphetanyl (I) was prepared from tert-butylphosphine via phosphine-boranes as intermediates. The rhodium

complex of the ligand was used as a highly efficient catalyst in asym. hydrogenations of α-acetyl-aminoacrylates and α-substituted enamides.

IT 735288-40-1P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and ligand use of DiSquareP* via heterocyclization of t-butylphosphine with dichloropropane followed by sulfurization, sparteine-catalyzed stereoselective dimerization, and desulfurization)

RN 735288-40-1 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'R,2R,2'R)- (9CI) (CA INDEX NAME)

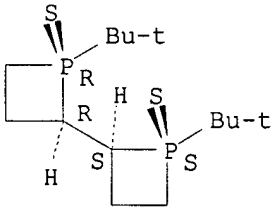
Absolute stereochemistry. Rotation (-).



IT 735288-42-3P
RL: SPN (Synthetic preparation); PREP (Preparation)
(stereoselective preparation of di(t-butyl)diphosphetanyl disulfide via heterocyclization of t-butylphosphine with dichloropropane followed by sulfurization and sparteine-catalyzed stereoselective dimerization)

RN 735288-42-3 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'S,2S,2'R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



REFERENCE COUNT: 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

FILE COVERS 1907 - 22 Jan 2007 VOL 146 ISS 5
FILE LAST UPDATED: 21 Jan 2007 (20070121/ED)

Effective October 17, 2005, revised CAS Information Use Policies apply. They are available for your review at:

http://www.cas.org/infopolicy.html

=> D L1
L1 HAS NO ANSWERS
L1 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.

=> S L1 FULL
REG1stRY INITIATED
Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

FULL SEARCH INITIATED 09:53:06 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 659 TO ITERATE

100.0% PROCESSED 659 ITERATIONS 6 ANSWERS
SEARCH TIME: 00.00.01

L3 6 SEA SSS FUL L1

L4 5 L3

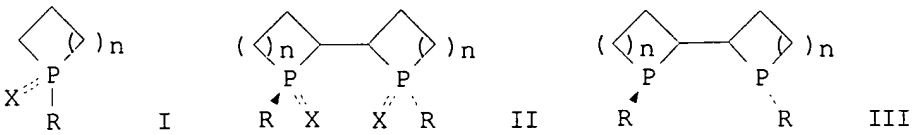
=> D L4 IBIB ABS HITSTR 1-5

L4 ANSWER 1 OF 5 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2005:99512 CAPLUS
DOCUMENT NUMBER: 142:198205
TITLE: Process for producing optically active dimer of phosphorus heterocycle
INVENTOR(S): Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S): Nippon Chemical Industrial Co., Ltd., Japan
SOURCE: PCT Int. Appl., 42 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent

LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.		DATE
WO 2005010014	A1	20050203	WO 2004-JP10671		20040727
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW					
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG					
EP 1650216	A1	20060426	EP 2004-747983		20040727
R: CH, DE, GB, LI					
US 2006211888	A1	20060921	US 2006-564985		20060118
PRIORITY APPLN. INFO.:			JP 2003-280584	A	20030728
			WO 2004-JP10671	W	20040727

OTHER SOURCE(S): MARPAT 142:198205
GI



AB A compound represented by the following general formula Y-CnH2n-Y (wherein Y = halogeno or a leaving group selected among -OTs, -OTf, and -OMs; n = a number of 3 to 6) is caused to act on a primary phosphine represented by the following general formula R-PH2 (wherein R = linear, branched, or cyclic C2-20 alkyl) in the presence of a base. Subsequently, boron trihydride, oxygen, or sulfur is caused to act thereon to obtain a heterocyclic phosphorus compound represented by the following general formula (I) (wherein R = the same as defined above; n = a number of 1 to 4; X = a boron trihydride group, oxygen, or sulfur; and = = = indicates a single bond when X is a boron trihydride group, and indicates a double bond when X is oxygen or sulfur). The compound I is dimerized to obtain a dimer of the heterocyclic phosphorus compound, the dimer being a diphosphetane represented by the following general formula (II) (wherein R, n, and X are the same as defined above). Subsequently, the phosphorus heterocycle dimer II is subjected to deoxidn., desulfurization, or borane elimination to obtain an optically active phosphorus heterocycle dimer represented by the following general formula (III) (wherein R and n are the same as defined above). These diphosphetanes III build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a

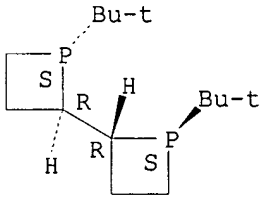
solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over 2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% III (R = tert-butyl). III (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol [rhodium(I)bis (norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice, 20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

IT 528814-24-6P
RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)

RN 528814-24-6 CAPLUS

CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, (1S,1'S,2R,2'R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

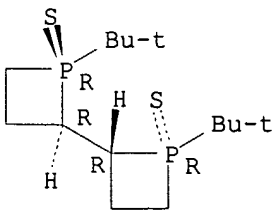


IT 735288-40-1P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)

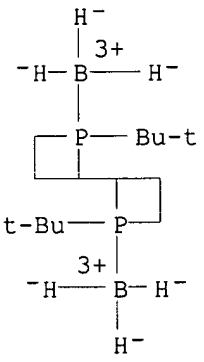
RN 735288-40-1 CAPLUS

CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'R,2R,2'R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

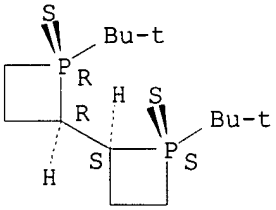


IT 735288-29-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)
RN 735288-29-6 CAPLUS
CN Boron, [μ-[(1S,1'S,2R,2'R)-1,1'-bis(1,1-dimethylethyl)-2,2'-biphosphetane-κP1:κP1']]hexahydrodi- (9CI) (CA INDEX NAME)



IT 735288-42-3P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)
RN 735288-42-3 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'S,2S,2'R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 5 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2005:99511 CAPLUS
DOCUMENT NUMBER: 142:198204
TITLE: Preparation of novel optically active phosphorus-chiral diphosphetanes, intermediates of the same, and transition metal complexes containing the diphosphetanes as the ligand
INVENTOR(S): Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S): Nippon Chemical Industrial Co., Ltd., Japan
SOURCE: PCT Int. Appl., 31 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 2

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.		DATE
WO 2005010013	A1	20050203	WO 2004-JP10670		20040727
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW					
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG					
EP 1650217	A1	20060426	EP 2004-770961		20040727
R: CH, DE, GB, LI					
US 2006189818	A1	20060824	US 2006-564984		20060118
PRIORITY APPLN. INFO.:			JP 2003-280584	A	20030728
			WO 2004-JP10670	W	20040727

OTHER SOURCE(S): MARPAT 142:198204

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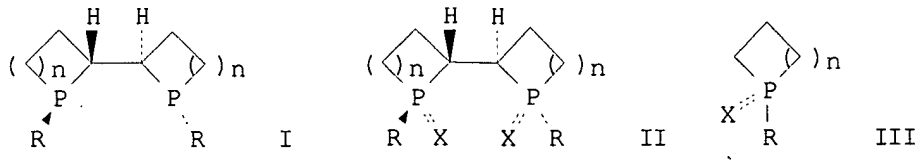


AB Novel optically active phosphorus-chiral diphosphetanes (I) (R = C2-20 straight-chain, branched, or cyclic alkyl) and intermediates of the same (II) and (III) (R = same as above; X = BH3, O, S; the double dotted line = a single bond when X = BH3 or a double bond when X = O or S), and transition metal complex catalysts containing the diphosphetanes as the ligand I are prepared These diphosphetanes build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over 2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% I (R = tert-butyl). I (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol [rhodium(I)bis(norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice,

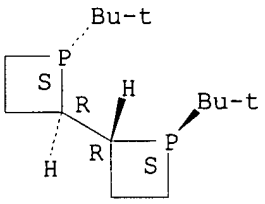
20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(nor bornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norborn adiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

IT 528814-24-6P, (1S,1S',2R,2R')-1,1'-Di-tert-butyl[2,2']diphosphetane
RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)
(preparation of novel optically active phosphorus-chiral diphosphetanes and transition metal complexes thereof for catalytic asym. syntheses such as asym. hydrogenation)

RN 528814-24-6 CAPLUS

CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, (1S,1'S,2R,2'R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

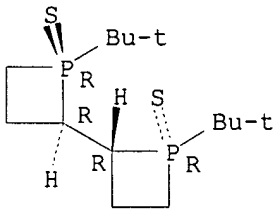


IT 735288-40-1P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of novel optically active phosphorus-chiral diphosphetanes and transition metal complexes thereof for catalytic asym. syntheses such as asym. hydrogenation)

RN 735288-40-1 CAPLUS

CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'R,2R,2'R)- (9CI) (CA INDEX NAME)

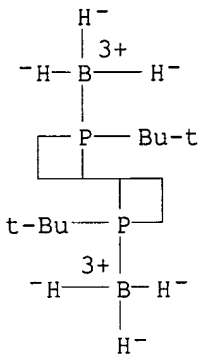
Absolute stereochemistry. Rotation (-).



IT 735288-29-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of novel optically active phosphorus-chiral diphosphetanes and transition metal complexes thereof for catalytic asym. syntheses such as asym. hydrogenation)

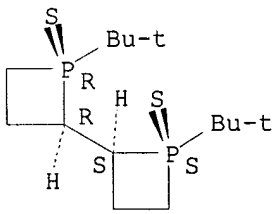
RN 735288-29-6 CAPLUS

CN Boron, [μ-[(1S,1'S,2R,2'R)-1,1'-bis(1,1-dimethylethyl)-2,2'-biphosphetane-κP1:κP1']]hexahydrodi- (9CI) (CA INDEX NAME)



IT 735288-42-3P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of novel optically active phosphorus-chiral diphosphetanes and transition metal complexes thereof for catalytic asym. syntheses such as asym. hydrogenation)
RN 735288-42-3 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'S,2S,2'R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 3 OF 5 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2004:995769 CAPLUS
DOCUMENT NUMBER: 141:424300
TITLE: P-chiral phospholanes and phosphocyclic compounds and their use in asymmetric catalytic reactions
INVENTOR(S): Zhang, Xumu; Tang, Wenjun
PATENT ASSIGNEE(S): The Penn State Research Foundation, USA
SOURCE: U.S. Pat. Appl. Publ., 41 pp., Cont.-in-part of U.S. Ser. No. 291,232.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2004229846	A1	20041118	US 2004-856014	20040528
US 2003144137	A1	20030731	US 2002-291232	20021108
US 7105702	B2	20060912		
US 2005119495	A1	20050602	US 2005-31159	20050107
US 7153809	B2	20061226		
WO 2005117907	A2	20051215	WO 2005-US14438	20050428
WO 2005117907	A3	20060908		

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH,

CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,
GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ,
LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA,
NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL,
SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA,
ZM, ZW
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,
AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT,
RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,
MR, NE, SN, TD, TG

PRIORITY APPLN. INFO.: US 2001-336939P P 20011109
US 2002-291232 A2 20021108
US 2004-856014 A3 20040528

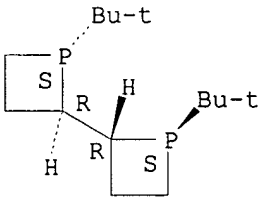
OTHER SOURCE(S): CASREACT 141:424300; MARPAT 141:424300

AB Chiral ligands and metal complexes based on such chiral ligands useful in asym. catalysis are disclosed. The metal complexes according to the present invention are useful as catalysts in asym. reactions, such as, hydrogenation, hydride transfer, allylic alkylation, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, olefin metathesis, hydrocarboxylation, isomerization, cyclopropanation, Diels-Alder reaction, Heck reaction, isomerization, Aldol reaction, Michael addition; epoxidn., kinetic resolution and [m+n] cycloaddn. Processes for the preparation of the ligands are also described. Thus, preparation of (1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphospholanyl TangPhos was prepared starting from 1,4-dibromobutane, PCl3, and t-BuMgCl and was used as cocatalyst with [Rh(NBD)2]SbF6 for asym. hydrogenation for dehydroamino acids.

IT 528814-24-6P 795290-32-3P
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(preparation of P-chiral phospholanes and phosphocyclic compds. and their use in transition metal catalyzed asym. reactions)

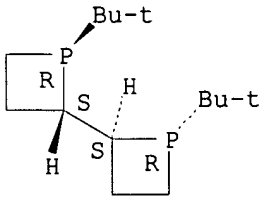
RN 528814-24-6 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, (1S,1'S,2R,2'R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



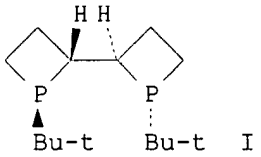
RN 795290-32-3 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, (1R,1'R,2S,2'S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L4 ANSWER 4 OF 5 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2004:536413 CAPLUS
DOCUMENT NUMBER: 141:174232
TITLE: Optically active 1,1'-di-tert-butyl-2,2'-diphosphetanyl and its application in rhodium-catalyzed asymmetric hydrogenations
AUTHOR(S): Imamoto, Tsuneo; Oohara, Nobuhiko; Takahashi, Hidetoshi
CORPORATE SOURCE: Department of Chemistry, Faculty of Science, Chiba University, Chiba, 263-8522, Japan
SOURCE: Synthesis (2004), (9), 1353-1358
CODEN: SYNTBF; ISSN: 0039-7881
PUBLISHER: Georg Thieme Verlag
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 141:174232
GI

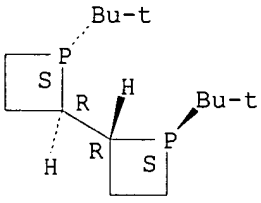


I

AB (1S,1'S,2R,2'R)-1,1'-Di-tert-butyl-2,2'-diphosphetanyl (I) was prepared from tert-butylphosphine via phosphine-boranes as intermediates. The rhodium complex of the ligand was used as a highly efficient catalyst in asym. hydrogenations of α-acetyl-aminoacrylates and α-substituted enamides.

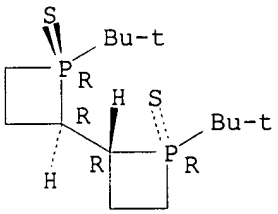
IT 528814-24-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and catalyst use of norbornadiene-DiSquareP*-rhodiums via deboronation of bis(phosphetane-borane) followed by complexation with bisnorbornadienerhodium)
RN 528814-24-6 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, (1S,1'S,2R,2'R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

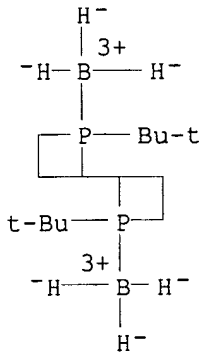


IT 735288-40-1P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and ligand use of DiSquareP* via heterocyclization of t-butylphosphine with dichloropropane followed by sulfurization, sparteine-catalyzed stereoselective dimerization, and desulfurization)
RN 735288-40-1 CAPLUS
CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'R,2R,2'R)- (9CI) (CA INDEX NAME)

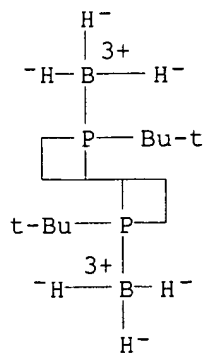
Absolute stereochemistry. Rotation (-).



IT 735288-29-6P
RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(stereoselective preparation and crystal structure of bis(phosphetane-borane) via heterocyclization of t-butylphosphine with dichloropropane followed by boronation and sparteine-catalyzed stereoselective dimerization in the preparation of DiSquareP*)
RN 735288-29-6 CAPLUS
CN Boron, [μ-[(1S,1'S,2R,2'R)-1,1'-bis(1,1-dimethylethyl)-2,2'-biphosphetane-κP1:κP1']]hexahydrodi- (9CI) (CA INDEX NAME)



IT 736140-19-5P
RL: SPN (Synthetic preparation); PREP (Preparation)
(stereoselective preparation of di(t-butyl)diphosphetanyl diborane via heterocyclization of t-butylphosphine with dichloropropane followed by addition of borane and sparteine-catalyzed stereoselective dimerization)
RN 736140-19-5 CAPLUS
CN Boron, [μ-[rel-(1R,1'S,2S,2'R)-1,1'-bis(1,1-dimethylethyl)-2,2'-biphosphetane-κP1:κP1']]hexahydrodi- (9CI) (CA INDEX NAME)



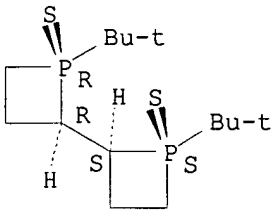
IT 735288-42-3P

RL: SPN (Synthetic preparation); PREP (Preparation)
(stereoselective preparation of di(t-butyl)diphosphetanyl disulfide via heterocyclization of t-butylphosphine with dichloropropane followed by sulfurization and sparteine-catalyzed stereoselective dimerization)

RN 735288-42-3 CAPLUS

CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, 1,1'-disulfide, (1R,1'S,2S,2'R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



REFERENCE COUNT: 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 5 OF 5 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:396818 CAPLUS

DOCUMENT NUMBER: 138:401901

TITLE: P-chiral phospholanes and phosphocyclic compounds and their use in asymmetric catalytic reactions

INVENTOR(S): Zhang, Xumu; Tang, Wenjun

PATENT ASSIGNEE(S): The Penn State Research Foundation, USA

SOURCE: PCT Int. Appl., 70 pp.
CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 2

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2003042135	A2	20030522	WO 2002-US35788	20021108
WO 2003042135	A3	20031224		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
CA 2466449	A1	20030522	CA 2002-2466449	20021108
AU 2002363788	A1	20030526	AU 2002-363788	20021108
EP 1451133	A2	20040901	EP 2002-803182	20021108
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK				
JP 2005509012	T	20050407	JP 2003-543975	20021108
CN 1608074	A	20050420	CN 2002-826029	20021108

PRIORITY APPLN. INFO.: US 2001-336939P P 20011109
WO 2002-US35788 W 20021108

OTHER SOURCE(S): CASREACT 138:401901; MARPAT 138:401901

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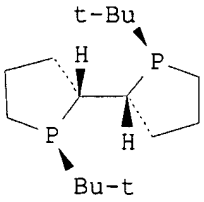


I

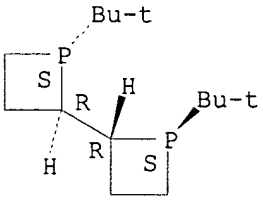
AB Chiral ligands and metal complexes based on such chiral ligands useful in asym. catalysis are disclosed. The metal complexes according to the present invention are useful as catalysts in asym. reactions, such as, hydrogenation, hydride transfer, allylic alkylation, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, olefin metathesis, hydrocarboxylation, isomerization, cyclopropanation. Diels-Alder reaction, Heck reaction, isomerization, Aldol reaction, Michael addition; epoxidn., kinetic resolution and [m+n] cycloaddn. Processes for the preparation of the ligands are also described. Thus, Grignard reaction of BrMgCH2(CH2)2CH2MgBr with PCl3 in the presence of t-BuMgCl in THF followed by thianation gave 1-tert-butylphospholane 1-sulfide which on BuLi/CuCl2-mediated coupling in presence of (-)-sparteine followed desulfurization with hexachlorodisilane/C6H6 gave title phospholane, TangPhos I. [Rh(COD)2]BF4-I mediated asym. catalytic reactions are described.

IT 528814-24-6P
RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)
(preparation of phosphorus-chiral phospholanes and related phosphocyclic compds. and their use as cocatalysts in asym. catalytic reactions)

RN 528814-24-6 CAPLUS

CN 2,2'-Biphosphetane, 1,1'-bis(1,1-dimethylethyl)-, (1S,1'S,2R,2'R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L6 3 L5

=> D L6 IBIB ABS HITSTR 1-3

L6 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER:	2005:99512 CAPLUS
DOCUMENT NUMBER:	142:198205
TITLE:	Process for producing optically active dimer of phosphorus heterocycle
INVENTOR(S):	Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S):	Nippon Chemical Industrial Co., Ltd., Japan
SOURCE:	PCT Int. Appl., 42 pp. CODEN: PIXXD2
DOCUMENT TYPE:	Patent
LANGUAGE:	Japanese
FAMILY ACC. NUM. COUNT:	2

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005010014	A1	20050203	WO 2004-JP10671	20040727
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1650216	A1	20060426	EP 2004-747983	20040727
R: CH, DE, GB, LI				
US 2006211888	A1	20060921	US 2006-564985	20060118
PRIORITY APPLN. INFO.:			JP 2003-280584 A	20030728
			WO 2004-JP10671 W	20040727
OTHER SOURCE(S):	MARPAT 142:198205			

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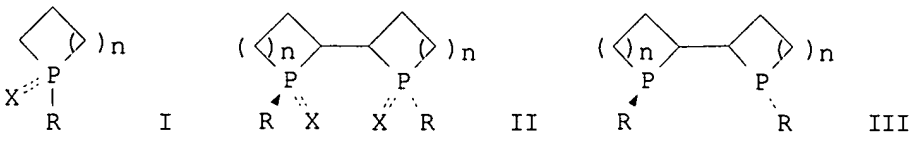
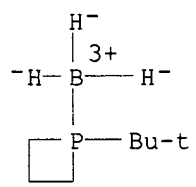


AB A compound represented by the following general formula Y-CnH2n-Y (wherein Y = halogeno or a leaving group selected among -OTs, -OTf, and -OMs; n = a number of 3 to 6) is caused to act on a primary phosphine represented by the following general formula R-PH2 (wherein R = linear, branched, or cyclic C2-20 alkyl) in the presence of a base. Subsequently, boron trihydride, oxygen, or sulfur is caused to act thereon to obtain a heterocyclic phosphorus compound represented by the following general formula (I) (wherein R = the same as defined above; n = a number of 1 to 4; X = a boron trihydride group, oxygen, or sulfur; and = = = indicates a single bond when X is a boron trihydride group, and indicates a double bond when X is oxygen or sulfur). The compound I is dimerized to obtain a dimer of the heterocyclic phosphorus compound, the dimer being a diphosphetane

represented by the following general formula (II) (wherein R, n, and X are the same as defined above). Subsequently, the phosphorus heterocycle dimer II is subjected to deoxidn., desulfurization, or borane elimination to obtain an optically active phosphorus heterocycle dimer represented by the following general formula (III) (wherein R and n are the same as defined above). These diphosphetanes III build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over 2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% III (R = tert-butyl). III (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol [rhodium(I)bis (norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice, 20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

IT 735288-28-5P
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)

RN 735288-28-5 CAPLUS
CN Boron, [1-(1,1-dimethylethyl)phosphetane]trihydro-, (T-4)- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2005:99511 CAPLUS

DOCUMENT NUMBER: 142:198204
TITLE: Preparation of novel optically active phosphorus-chiral diphosphetanes, intermediates of the same, and transition metal complexes containing the diphosphetanes as the ligand
INVENTOR(S): Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S): Nippon Chemical Industrial Co., Ltd., Japan
SOURCE: PCT Int. Appl., 31 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005010013	A1	20050203	WO 2004-JP10670	20040727
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1650217	A1	20060426	EP 2004-770961	20040727
R: CH, DE, GB, LI				
US 2006189818	A1	20060824	US 2006-564984	20060118

PRIORITY APPLN. INFO.: JP 2003-280584 A 20030728
WO 2004-JP10670 W 20040727

OTHER SOURCE(S): MARPAT 142:198204
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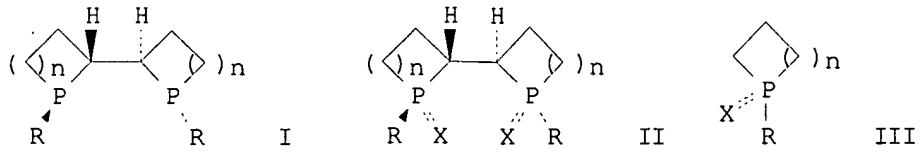
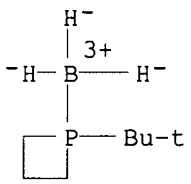


AB Novel optically active phosphorus-chiral diphosphetanes (I) (R = C2-20 straight-chain, branched, or cyclic alkyl) and intermediates of the same (II) and (III) (R = same as above; X = BH3, O, S; the double dotted line = a single bond when X = BH3 or a double bond when X = O or S), and transition metal complex catalysts containing the diphosphetanes as the ligand I are prepared These diphosphetanes build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over

2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% I (R = tert-butyl). I (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol [rhodium(I)bis(norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice, 20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

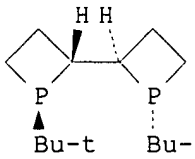
IT 735288-28-5P
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of novel optically active phosphorus-chiral diphosphetanes and transition metal complexes thereof for catalytic asym. syntheses such as asym. hydrogenation)

RN 735288-28-5 CAPLUS
CN Boron, [1-(1,1-dimethylethyl)phosphetane]trihydro-, (T-4)- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2004:536413 CAPLUS
DOCUMENT NUMBER: 141:174232
TITLE: Optically active 1,1'-di-tert-butyl-2,2'-diphosphetanyl and its application in rhodium-catalyzed asymmetric hydrogenations
AUTHOR(S): Imamoto, Tsuneo; Oohara, Nobuhiko; Takahashi, Hidetoshi
CORPORATE SOURCE: Department of Chemistry, Faculty of Science, Chiba University, Chiba, 263-8522, Japan
SOURCE: Synthesis (2004), (9), 1353-1358
CODEN: SYNTBF; ISSN: 0039-7881
PUBLISHER: Georg Thieme Verlag
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 141:174232
GI



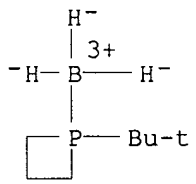
I

AB (1S,1'S,2R,2'R)-1,1'-Di-tert-butyl-2,2'-diphosphetanyl (I) was prepared from tert-butylphosphine via phosphine-boranes as intermediates. The rhodium complex of the ligand was used as a highly efficient catalyst in asym. hydrogenations of α-acetyl-aminoacrylates and α-substituted enamides.

IT 735288-28-5P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(stereoselective preparation and crystal structure of bis(phosphetane-borane) via heterocyclization of t-butylphosphine with dichloropropane followed by boronation and sparteine-catalyzed stereoselective dimerization in the preparation of DiSquareP*)

RN 735288-28-5 CAPLUS

CN Boron, [1-(1,1-dimethylethyl)phosphetane]trihydro-, (T-4)- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

FILE COVERS 1907 - 22 Jan 2007 VOL 146 ISS 5
FILE LAST UPDATED: 21 Jan 2007 (20070121/ED)

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http://www.cas.org/infopolicy.html

=> D L1
L1 HAS NO ANSWERS
L1 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.

=> S L1 FULL
REG1stRY INITIATED
Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

FULL SEARCH INITIATED 10:38:00 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 23554 TO ITERATE

100.0% PROCESSED 23554 ITERATIONS 1 ANSWERS
SEARCH TIME: 00.00.01

L3 1 SEA SSS FUL L1

L4 3 L3

=> D L4 IBIB ABS HITSTR 1-3

L4 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2005:99512 CAPLUS
DOCUMENT NUMBER: 142:198205
TITLE: Process for producing optically active dimer of phosphorus heterocycle
INVENTOR(S): Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S): Nippon Chemical Industrial Co., Ltd., Japan
SOURCE: PCT Int. Appl., 42 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent

LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005010014	A1	20050203	WO 2004-JP10671	20040727
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1650216	A1	20060426	EP 2004-747983	20040727
R: CH, DE, GB, LI				
US 2006211888	A1	20060921	US 2006-564985	20060118
PRIORITY APPLN. INFO.:			JP 2003-280584 A	20030728
			WO 2004-JP10671 W	20040727

OTHER SOURCE(S): MARPAT 142:198205
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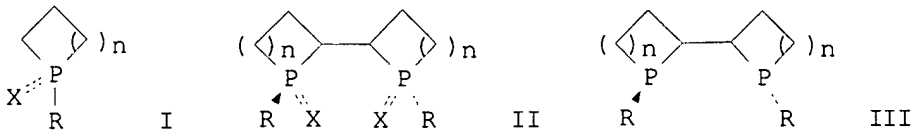
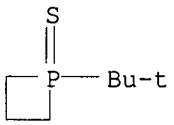


AB A compound represented by the following general formula Y-CnH2n-Y (wherein Y = halogeno or a leaving group selected among -OTs, -OTf, and -OMs; n = a number of 3 to 6) is caused to act on a primary phosphine represented by the following general formula R-PH2 (wherein R = linear, branched, or cyclic C2-20 alkyl) in the presence of a base. Subsequently, boron trihydride, oxygen, or sulfur is caused to act thereon to obtain a heterocyclic phosphorus compound represented by the following general formula (I) (wherein R = the same as defined above; n = a number of 1 to 4; X = a boron trihydride group, oxygen, or sulfur; and = = = indicates a single bond when X is a boron trihydride group, and indicates a double bond when X is oxygen or sulfur). The compound I is dimerized to obtain a dimer of the heterocyclic phosphorus compound, the dimer being a diphosphetane represented by the following general formula (II) (wherein R, n, and X are the same as defined above). Subsequently, the phosphorus heterocycle dimer II is subjected to deoxidn., desulfurization, or borane elimination to obtain an optically active phosphorus heterocycle dimer represented by the following general formula (III) (wherein R and n are the same as defined above). These diphosphetanes III build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a

solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over 2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% III (R = tert-butyl). III (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol [rhodium(I)bis (norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice, 20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

IT 735288-38-7P, 1-tert-Butylphosphetane-1-sulfide
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of novel optically active diphosphetanes and transition metal complexes thereof by cyclocondensation of tert-butylphosphine with dichloropropane and dimerization of phosphetane)

RN 735288-38-7 CAPLUS
CN Phosphetane, 1-(1,1-dimethylethyl)-, 1-sulfide (9CI) (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2005:99511 CAPLUS
DOCUMENT NUMBER: 142:198204
TITLE: Preparation of novel optically active phosphorus-chiral diphosphetanes, intermediates of the same, and transition metal complexes containing the diphosphetanes as the ligand
INVENTOR(S): Oohara, Nobuhiko; Imamoto, Tsuneo
PATENT ASSIGNEE(S): Nippon Chemical Industrial Co., Ltd., Japan
SOURCE: PCT Int. Appl., 31 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005010013	A1	20050203	WO 2004-JP10670	20040727

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI,
NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,
AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE,
SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE,
SN, TD, TG

EP 1650217	A1	20060426	EP 2004-770961		20040727
R: CH, DE, GB, LI					
US 2006189818	A1	20060824	US 2006-564984		20060118
PRIORITY APPLN. INFO.:			JP 2003-280584	A	20030728
			WO 2004-JP10670	W	20040727

OTHER SOURCE(S): MARPAT 142:198204

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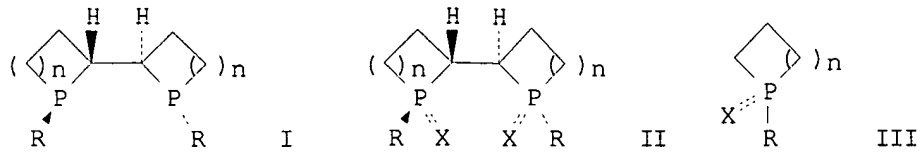
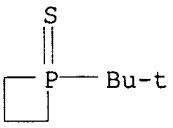


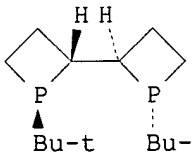
AB Novel optically active phosphorus-chiral diphosphetanes (I) (R = C2-20 straight-chain, branched, or cyclic alkyl) and intermediates of the same (II) and (III) (R = same as above; X = BH3, O, S; the double dotted line = a single bond when X = BH3 or a double bond when X = O or S), and transition metal complex catalysts containing the diphosphetanes as the ligand I are prepared These diphosphetanes build stable asym. spaces in coordinating to central metals and are useful as ligands of transition metal catalysts for catalytic asym. syntheses such as asym. hydrogenation. Thus, a solution of 200 mmol tert-butylphosphine and 200 mmol 1,3-dichloropropane in n-hexane and THF was cooled to -78°, treated dropwise with 277 mL 1.59 M BuLi/hexane (440 mmol) over 1 h, stirred at -78° for 1 h, warmed to room temperature, treated with 9.6 g (300 mmol) sulfur powder, and stirred at room temperature for 2 h to give, after workup and purification using an alumina column, 48% 1-tert-butylphosphentane-1-sulfide (IV). A mixture of 36 mmol sparteine and 70 mL Et2O was cooled to -78°, treated with 36 mmol s-BuLi, stirred for 1 h, treated with a solution of 30 mmol IV in 30 mL toluene at -78° over 1 h, stirred at -78° for 5 h, treated with 45 mmol CuCl, warmed to room temperature over 2 h, and stirred at room temperature for 12 h to give, after workup, purification by flash chromatog., and 4 recrystns. from EtOAc, 10% II (R = tert-Bu, X = S). II (R = tert-Bu, X = S) (0.4 mmol) was dissolved in 8 mL benzene, treated with 5.8 mmol hexachlorodisilane, refluxed for 3 h, cooled to 0°, carefully treated with 30% aqueous NaOH solution, heated at 50° with stirring to give, after workup and purification using an alumina column, 75% I (R = tert-butyl). I (R = tert-butyl) (0.3 mmol) was dissolve din 4 mL THF, cooled to 0°, added to a suspension of 0.27 mmol [rhodium(I)bis(norbornadiene)]tetrafluoroborate and 10 mL THF, stirred at room temperature for 3 h to give, after filtration through a celite column, evaporation of the filtrate, and washing the orange solid with 5 mL Et2O twice, 20% [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]tetrafluoroborate (V). Me α-acetamidocinnamate (1 mmol) was hydrogenated over 0.002 mmol V in methanol at room temperature for 4 h to give ≥99% D-phenylalanine Me ester (96.8% optical purity). Asym. hydrogenation of various dehydroamino acid derivs. or enamides using [rhodium(I)((1S,1S',2R,2R')-1,1'-di-tert-butyl[2,2']diphosphetane)(norbornadiene)]hexafluorophosphate gave (R)-α-amino acids and optically active amines.

IT 735288-38-7P, 1-tert-Butylphosphetane-1-sulfide
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of novel optically active phosphorus-chiral diphosphetanes and transition metal complexes thereof for catalytic asym. syntheses such as asym. hydrogenation)
RN 735288-38-7 CAPLUS
CN Phosphetane, 1-(1,1-dimethylethyl)-, 1-sulfide (9CI) (CA INDEX NAME)



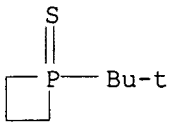
REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 2004:536413 CAPLUS
DOCUMENT NUMBER: 141:174232
TITLE: Optically active 1,1'-di-tert-butyl-2,2'-diphosphetanyl and its application in rhodium-catalyzed asymmetric hydrogenations
AUTHOR(S): Imamoto, Tsuneo; Oohara, Nobuhiko; Takahashi, Hidetoshi
CORPORATE SOURCE: Department of Chemistry, Faculty of Science, Chiba University, Chiba, 263-8522, Japan
SOURCE: Synthesis (2004), (9), 1353-1358
CODEN: SYNTBF; ISSN: 0039-7881
PUBLISHER: Georg Thieme Verlag
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 141:174232
GI



I

AB (1S,1'S,2R,2'R)-1,1'-Di-tert-butyl-2,2'-diphosphetanyl (I) was prepared from tert-butylphosphine via phosphine-boranes as intermediates. The rhodium complex of the ligand was used as a highly efficient catalyst in asym. hydrogenations of α-acetyl-aminoacrylates and α-substituted enamides.
IT 735288-38-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and ligand use of DiSquareP* via heterocyclization of t-butylphosphine with dichloropropane followed by sulfurization, sparteine-catalyzed stereoselective dimerization, and desulfurization)
RN 735288-38-7 CAPLUS
CN Phosphetane, 1-(1,1-dimethylethyl)-, 1-sulfide (9CI) (CA INDEX NAME)



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